



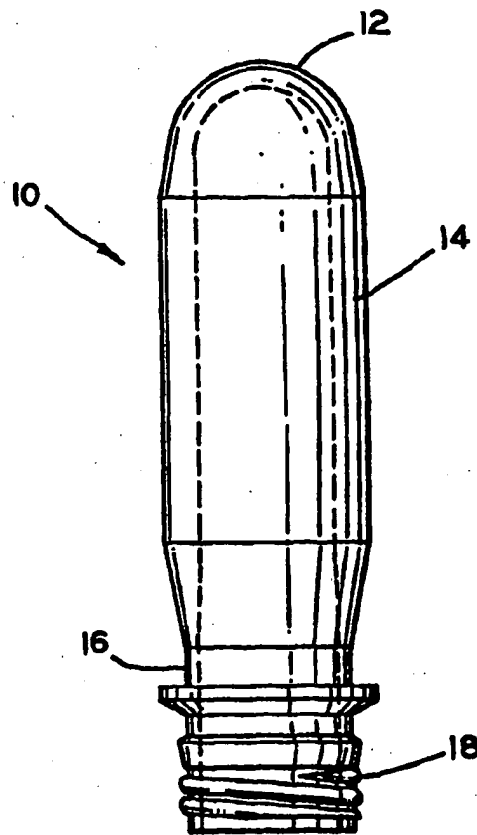
## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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| (51) International Patent Classification <sup>6</sup> :<br><b>B29C 45/00, 49/00, 49/64</b>  | <b>A2</b> | (11) International Publication Number: <b>WO 95/11791</b>   |
|   |           | (43) International Publication Date: <b>4 May 1995 (04.05.95)</b>   |
| <p>(21) International Application Number: <b>PCT/EP94/03525</b></p> <p>(22) International Filing Date: <b>26 October 1994 (26.10.94)</b></p> <p>(30) Priority Data:<br/><b>08/144,204</b>      <b>27 October 1993 (27.10.93)</b>      <b>US</b></p> <p>(71) Applicant: <b>BEKUM MASCHINENFABRIKEN GMBH</b><br/><b>[DE/DE]; Lankwitzer Strasse 14-15, D-12107 Berlin (DE).</b></p> <p>(72) Inventors: <b>GITTNER, Franz; Im Grundfeld 33, D-29594</b><br/><b>Soltendieck (DE). ROOS, Uwe-Volker; Hasenheide 12, D-</b><br/><b>29389 Bodenteich (DE). STEELE, Scott, W.; Toledo, Ohio,</b><br/><b>1465 Timberwolf Drive, Holland, OH 43528-0964 (US).</b></p> <p>(74) Agent: <b>FLOSDORFF, Jürgen; Alleestrasse 33, D-82467</b><br/><b>Garmisch-Partenkirchen (DE).</b></p> |           | <p>(81) Designated States: <b>AU, BR, CA, JP, KR, PL, European patent</b><br/><b>(AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC,</b><br/><b>NL, PT, SE).</b></p> <p><b>Published</b><br/><i>Without international search report and to be republished<br/>upon receipt of that report.</i></p> |

(54) Title: METHOD OF FORMING MOLECULARLY ORIENTED CONTAINERS

## (57) Abstract

The invention relates to a method and apparatus for forming molecularly oriented plastic containers from generally cylindrical, hollow preforms with one open end formed by injection molding from a partially crystalline, molecularly orientable plastic for subsequent stretch blow molding. Melted material is injected into a preform mold at a predetermined fill rate controlled to minimize molecular flow orientation and further controlled to minimize residual stress which both are otherwise developed during injection. The preform is then reheated below the crystal melting point by radiant heat source to a temperature that intercrystalline structures are melted without melting the crystal nuclei. To avoid so-called edge effects resulting from the geometry of the heating zone, the preform decreases in thickness at both ends. The preform is then rapidly transferred to the mold in which it is stretched axially with a rod engaging its closed end and then rapidly quenched against a polished mold surface.



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**TITLE****METHOD OF FORMING MOLECULARLY ORIENTED CONTAINERS**

5

**BACKGROUND OF THE INVENTION****1. Field of the Invention**

The present invention relates to a method and apparatus for forming molecularly oriented plastic containers and, more particularly, to a method and apparatus for forming oriented containers from a polypropylene containing polymer by a reheat, stretch blow molding process.

**2. Summary of Related Art**

Stretch blow molding has rapidly gained acceptance as a method of producing oriented plastic containers over a wide range of shapes and sizes. In stretch blow molding, a parison or preform is first formed by either an extrusion or injection molding operation, subsequently stretched, either mechanically or otherwise, and blown in both an axial and radial direction. In so doing, the molecules are aligned along two planes, an arrangement that advantageously improves clarity, impact strength, gas and water vapor barrier properties, and stiffness in the finished container. The resulting containers are lighter weight, resulting in a substantial savings in the amounts of resin used. The amounts of processing additives otherwise required may also be reduced.

The resins normally considered for stretch blow molding include: polyethylene terephthalate (PET), polyvinyl chloride (PVC), polypropylene (PP), high density polyethylene (HDPE) and acrylonitrile copolymers (PAN). Currently, PET is the most widely used, especially in food packaging applications. However, PET lacks hot fill

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capability and is a relatively high cost material.

5 Biaxially oriented PP is a potentially lower cost alternative which exhibits good hot fill capability. Nonetheless, oriented PP containers have never really achieved a high degree of commercial success. This has been due in part to the fact that conventional methods of stretch blow molding PP have resulted in containers having only fair optical clarity. More importantly, conventional PP stretch blow molding processes have not been economically attractive, since none of these processes has attained the extremely precise temperature control required to obtain orientation of PP, except by using very long heating times.

15 There are basically two types of processes for stretch blow molding: 1) the single stage process in which preforms are first made and then allowed to cool to the correct blow molding temperature before being blown into containers on the same machine; and 2) the two-stage process in which preforms first are made on one machine, allowed to cool to room temperature outside of that machine, and then reheated and blown on another machine. Two-stage extrusion type machines have generally been used to make oriented PP preforms and containers. In such a process, preforms are generally extruded, cooled, cut to length, reheated, stretched while the neck finish is being compression molded, then blown, trimmed and ejected.

30 The reheating of the PP preform is critical because a precise preform temperature must be achieved at which intercrystalline material begins to melt, but at which the crystallites themselves do not melt. Thus, the PP preform must achieve a uniform temperature just below its peak

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crystalline melting point. Any increase in temperature above this point will cause the crystallites to melt and thereby eliminate any possibility of obtaining optimum orientation during the subsequent stretch blow molding operation. This effect is particularly important for preforms of PP containing resins, and is still not well understood in the industry. In any event, the result has been that conventional reheat methods have used ovens set at the exact final temperature desired for the preform. As those skilled in the art will appreciate, with such heater settings, as the actual average preform temperature approaches the final desired temperature, the driving force to continue any temperature increase in the preform decreases. The result is that a very long time is required to asymptotically approach the final desired temperature and, in practice, this final desired temperature is never quite realized.

Various reheating methods have been described relative to the blow molding of oriented PP containers. Examples include Wiley's U.S. Patent Nos. 3,496,258 and Re. 26,956, and Seeluth's U.S. Patent No. 3,950,459. In the above cited patents, Wiley discloses a method of conditioning an extruded tube of thermoplastic prior to orientation thereof by blow molding. The reheating of the extruded tube is controlled so that the exterior portion of the tube is in a crystalline condition and is oriented, while the inside of the tube is maintained relatively tacky and in a sealable condition. According to Wiley, after the preform is extruded, the outer surface is cooled until it reaches a crystalline state. Then, the outer surface is reheated to bring the temperature of the outer

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surface to within a few degrees of the crystal melting point. The heat flow is reduced to leave the inside of the preform in a tacky, sealable condition. The reheated preform is then stretch blow molded in the conventional manner. Since the Wiley preform is not at proper orientation temperature throughout its wall thickness, orientation is not achieved throughout the wall thickness and the clarity of the product suffers accordingly.

Seeluth, in U.S. Patent No. 3,950,459, discloses a method of producing a preform and blow molding the preform, wherein a tubular preform is extruded and cooled to below its orientation temperature. The preforms are then passed through a heating zone maintained at an elevated temperature, keeping the preforms free of any angular rotation, to heat the preform to an average temperature within the orientation range. In a second heating zone, Seeluth teaches directing radiant energy on at least three peripheral radial portions of each preform, so that each portion is heated to a different orientation temperature. The preforms are blow molded and the wall thickness in each of the portions is measured. The amount of radiant energy applied to the various portions of the preforms is adjusted in response to these measurements.

As noted above, the two-stage processes may also use preforms which are injection molded on multicavity molds, then cooled to ambient temperatures before introduction into a reheat-blow molding machine. Injection molding of the preforms provides certain advantages over extrusion of the preforms. In contrast to the tubular extruded preforms, the molds for injection molded preforms may be formed in the desired final shape. Furthermore, injection

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molding eliminates the need to close the end of each preform as required with extruded preforms.

Oas et al., for example, in the U.S. Patent N . 4,357,288, disclose a method of forming PP preforms by an injection molding operation. The melt temperatures of the plastics material are controlled to be just slightly above the melting point index of the PP formulations. These temperatures are said to be sufficiently above the crystalline melt temperature to avoid melt fractures during injection and sufficiently below the temperature at which the PP formulations will degrade. The preform is stripped from the mold, heated to a temperature just below its amorphous flow temperature, and then placed in a stretch blow molding apparatus.

Despite the efforts of those skilled in the art, an efficient method of forming molecularly oriented polypropylene containers having satisfactory clarity was heretofore unavailable.

#### SUMMARY OF THE INVENTION

The present invention relates to an improved method and apparatus for forming molecularly oriented plastic containers. A generally cylindrical, hollow preform having a closed end and an open end is preferably formed by injection molding from a partially crystalline, molecularly orientable plastic for subsequent stretch blow molding. Melted material is injected into a preform mold cavity at a predetermined fill rate which is controlled so as to minimize molecular flow orientation induced in the plastic material by the injection thereof into the mold. The injection fill rate is also controlled so as to

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minimize residual stress which would otherwise be developed in the plastic material during injection.

The preform is then reheated prior to the stretch blow molding operation to a temperature below the crystal melting point of the material. The preform is preferably passed through a series of heating zones each containing a radiant heat source which heats the preform to a temperature at which intercrystalline structures in the preform are melted without melting the crystal nuclei which were connected by the intercrystalline regions. To avoid so-called edge effects which result from the geometry of the heating zone, it has been found to be advantageous to form the injection molding cavity so that the resulting preform decreases in thickness at both ends thereof.

The preform is then rapidly transferred to the molding zone and secured within the mold of a stretch blow molding apparatus. The preform is stretched axially with an internal stretch rod which engages the closed end of the preform, and a pressure differential is created which is sufficient to expand the preform into conformity with the walls of the mold. The preform is rapidly quenched against a polished mold surface to produce a molecularly oriented container having improved clarity, impact strength, gas and water vapor barrier properties, and stiffness.

An object of the present invention, therefore, is to provide a molecularly oriented plastic container having improved clarity;



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A further object is to provide a method for producing such a molecularly oriented plastic container in a time and cost efficient manner;

5 Another object of the invention is to provide an improved method of forming the preforms for subsequent stretch blow molding of such molecularly oriented plastic containers;

10 A still further object is to provide an improved method of reheating the preforms immediately prior to stretch blow molding such molecularly oriented plastic container;

Another object of the invention is to provide an improved method of stretch blow molding reheated preforms to produce such molecularly oriented plastic containers;

15 Other objects and advantages will become more apparent during the course of the following description when taken in connection with the accompanying drawings.

#### BRIEF DESCRIPTION OF THE DRAWINGS

20 The above, as well as other advantages of the present invention, will become readily apparent to those skilled in the art from the following detailed description of a preferred embodiment when considered in the light of the accompanying drawings in which:

25 Fig. 1 is a longitudinal sectional view of a preform in accordance with the present invention; and

Fig. 2 is a schematic, overhead view of a portion of the reheat system of the invention.

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DESCRIPTION OF THE PREFERRED EMBODIMENT

In accordance with the present invention, a preform is first formed by the injection molding of a partially crystalline, molecularly orientable plastic, subsequently reheated, then stretched and blown in both an axial and radial direction, and rapidly quenched. In so doing, the molecules are preferentially aligned along two planes, an arrangement that advantageously improves clarity, impact strength, gas and water vapor barrier properties, and stiffness in the finished container.

The methods of the present invention may be employed to form molecularly oriented containers of any partially crystalline, molecularly orientable plastic. Exemplary polymers are polymers of at least one mono-1-olefin having 2-8 carbon atoms per molecule. Polypropylene containing materials are preferred, examples of which include PP homopolymers, copolymers which contain more than 50% by weight propylene, or a mixture of polypropylene homopolymers or said copolymers with at least one material such as polyethylene, polybutene, poly-4-methylpentene-1 and elastomeric ethylene/propylene copolymer. Suitable PP containing resins according to the invention can contain lubricants, pigments, dyes, inorganic or organic fillers, polymer additives or other additives which are conventionally used in resins to be blow molded.

A particularly preferred material for use in accordance with the present invention is a propylene/ethylene copolymer which is greater than 50% by weight propylene. The melt index of the propylene/ethylene copolymer is from about 2 to about 50, and is preferably from about 10 to 30.

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It has been determined that the preform design and crystal morphology, the method of reheating and heating zone geometry, and methods of stretch-blow molding all influence the quality of the container obtained.

- 5 Improvements in each step of the overall process have been discovered, and the present invention thus provides a method of producing oriented PP containers having good clarity, without unduly long cycle times.

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#### 1. PRODUCING THE PREFORM

- It is known that an injected molded preform must have the correct crystal morphology to properly orient during the stretch blow molding operation. That is, the crystal structures should be uniformly distributed throughout the preform and the crystallites should be relatively small. 15 It has been determined that the preform crystal morphology is dependent upon the injection molding conditions.

- In accordance with the present invention, a closed-ended preform is injection molded from a partially 20 crystalline, molecularly orientable plastic. The injection molding of the preforms is carried out under process conditions which produce minimal flow orientation due to the injection filling process, resulting in crystal structures uniformly distributed throughout the preform and of relatively of small dimensions. 25

- It has also been determined that it is important for the preform to be substantially stress-free. Residual stress has at least two undesirable effects. First, when a stressed preform becomes partially molten as it is 30 reheated to a temperature below the crystal melting point, the shape of the preform can change substantially as the

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internal stresses are relieved. Should this occur, the preform will become measurably shorter and the walls will become thicker, and the preform will become much more difficult to reheat uniformly and optimally by conventional radiant energy methods. In addition, residual stresses can induce an increase in the rate of recrystallization upon reheating. This effect also can interfere with achieving optimum clarity.

Best results have been achieved at fill rates of from about 3 to about 5 grams per second for a single injection cavity, followed by rapid quenching at cooling rates of 4 to 8 °C/sec. Injection rates above about 5 grams per second result in residual stresses which detrimentally effect the clarity of the subsequently formed container. Injection rates below about 3 grams per second result in a significant number of short shots, and may also cause detrimentally high residual stresses in the preform.

The melt is preferably injected into a mold cavity having chilled mold surfaces which are maintained in a temperature range of between about 5 to 20°C. These conditions have been found to produce a uniformly distributed crystal structure and relatively small crystallite dimensions.

The melt is introduced into the preform cavity at the closed end of the preform and is forced to fill out the remaining cavity by the corresponding injection pressure. Either cold runner or hot runner injection molds, and either thermal or mechanical shut off devices may be employed. In addition, the exact geometry of the melt flow channels does not seem to be critical, so long as a

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good balance of flow and cooling are achieved between preforms from cavity to cavity.

Because the geometry of the typical reheating system influences the heat pattern along the length of the preform, it has been determined that the wall thickness of the preform must vary along its entire length in order to compensate for the variations in the energy which impinges upon the preform and which is imposed by the heating system design itself. As illustrated in Figure 1, a generally cylindrical, hollow preform 10 is formed with a closed end 12, a main body portion 14, a neck 16 and a threaded open end 18. The preform walls at both the closed end 12 and the neck 16 are thinner than the preform wall forming the main body portion 14, to compensate for the fact that the energy intensity is lower at the edges of a heater panel. This variation in the heat absorption and the resulting change in the axial temperature profile according to the change in axial thickness has been found to be important in creating a uniform resistance to blowing over the entire length of the preform. This results in a reheated preform which is more uniform in strength along the length of the preform.

The variation in the wall thickness of the preform is most easily obtained by forming the injection mold cavity so that the resulting preform decreases in thickness at both of the ends thereof. The preform is formed with a decrease in thickness at both of the ends thereof of between about 40 to 70 percent. To produce a typical molecularly oriented container, the preform may be formed with a decrease in thickness from about 5mm in the middle to about 3mm at both of the ends thereof.

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## 2. REHEATING THE PREFORMS

Once a preform has been produced having the desired geometry and crystal morphology, the preform is allowed to cool to a substantially uniform temperature which is at least below the temperature at which the melting of crystals in the material begins. The preforms are generally allowed to cool to ambient temperature. The preforms then must be reheated prior to the stretch blow molding operation.

The reheating of a partially crystalline molecularly orientable plastic, particularly PP, preform prior to stretch blow molding is critical. This is because a precise preform temperature must be achieved which is uniform throughout the preform wall and at which intercrystalline material melts, but at which the crystallites or crystal nuclei themselves do not melt. Thus, the PP preform must be brought to a temperature just below its peak crystalline melting point. Further, the temperature across the entire wall thickness of the preform must be brought within this relatively narrow temperature range in order to achieve optimum orientation and container clarity. Any increase in temperature above this point will cause the crystallites to melt, thereby eliminating any possibility of obtaining optimum orientation during the subsequent stretch blow molding operation.

The preform is preferably exposed to a zone-controlled array of infra-red heaters to reheat the preform to a temperature just below the crystal melting point of the material. It has been found that PP is largely transparent to IR energy at wavelengths of 1.2 to

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1.6 microns. Therefore, heating a relatively thick preform with IR energy which is not readily absorbed by the preform results in rapid and uniform heating through the wall thickness, even though this process itself is fundamentally inefficient from a total energy absorption viewpoint. The heating system is designed to partially melt the polypropylene crystals, leaving a fine structure of crystal nuclei for subsequent crystallization during the stretching/orientation process.

It has also been discovered that the latent heat of crystallization of the PP can be utilized to "buffer" the over-heating condition in combination with cooling air which is directed over the surface of the preform while the preform is within the heating zone. That is, the preforms are introduced to an IR heating array while simultaneously being subjected to surface cooling air to prevent overheating/melting of the exterior wall of the preforms. The amount of heat absorbed at the outside surface is higher than the heat absorbed by the underlying layers, which results in the outside surface being heated to a higher temperature more quickly than the underlying layers.

As illustrated schematically in Figure 2, the preforms 10 are loaded onto a series of rotating mandrels mounted to a conveyor chain 20 which transports the preforms 10 through the following heating steps. The preforms are maintained in proximity to a first IR heating panel 22 until the temperature of the preform near its exterior surface exceeds the temperature at which the intercrystalline material begins to melt, and begins to approach the temperature at which all crystalline material

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near the exterior surface is melted. As noted above, however, this overheating condition is partially controlled by the fact that the crystal melting is an endothermic process, and for a short time the additional heat being absorbed at the surface of the preforms does not cause a temperature rise. The heating panels all preferably comprise high intensity, quartz tubular IR heating panels.

A reflective shield 24, preferably formed of a sheet of highly polished aluminum, extends substantially the length of the conveyor chain and is parallel to each of the heating panels with the conveyor chain running approximately midway therebetween. The reflector shield is provided with slots which communicate with a series of cooling air supply ducts 26a-26f and serve to direct cooling air to the exterior surface of the preforms. There is preferably a separate duct for each heating and cooling zone, so that the amount of cooling air can be separately controlled for each zone.

The preforms are removed from the first heating panel 22 and introduced to a cooling zone 23 where a second source of cooling gas, preferably air at ambient temperature, is supplied through duct 26b in order to allow the temperature gradient developed across the wall thickness of the preforms to substantially equalize by thermal conduction. The amount of cooling air employed during this stage is greater than that employed while the preforms are adjacent the heating panel which is supplied by duct 26a, but cannot be so excessive so as to re quench the surface of the preform, since doing so could detract from the final clarity of the blown bottles.



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These reheating and cooling steps are repeated at least once more, and most preferably two more times, by advancing the preforms by addition IR heating panels 28 and 30, the latter having a relatively lower heating intensity than the initial heating panel, and followed by associated cooling zones 29 and 31. During the cooling steps, the temperature of the preform near its exterior surface is lowered, while the inner layers of the preform wall continue to rise in temperature. Thus, the average temperature of the preform rises relatively rapidly, while the temperature gradient across the wall of the preform decreases, as the preform advances through the reheat system.

The preforms are then preferably introduced into an air convection tempering oven which is set at the temperature desired for orientation upon stretch blow molding, which is a temperature above the temperature at which intercrystalline structures on the preform begin to melt, but below the temperature at which all crystal structures in the preform are melted. The preforms remain in the oven for a time sufficient to allow any remaining temperature gradient which was developed across the thickness of the preform to substantially equalize.

The preforms, having been uniformly reheated to a proper orientation temperature, are rapidly transferred to a stretch blow molding apparatus.

### 3. STRETCH BLOW MOLDING THE PREFORMS

Once reheated to the desired orientation temperature, the preform is immediately positioned in the known manner within the mold cavity of the stretch blow molding

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apparatus. The preform is stretched axially by employing an internal stretch rod which engages the closed end of the preform. The preform is stretched radially by introducing internal blowing pressure at the open end of the preform until the preform is in conformity with the walls of the mold cavity.

The axially stretching and radial blowing of the preform may be carried either sequentially or simultaneously. In accordance with a preferred embodiment of the present invention, axial stretching is provided by an internal stretch rod which is operated at rates of between about 110 cm/sec and 330 cm/sec, and preferably about 170 cm/sec and 270 cm/sec. Some volume of blowing air is simultaneously introduced into the open end of the preform to radially expand the preform and conform the preform substantially to the mold. After the stretch rod is fully extended, a higher blowing pressure is introduced for the purpose of completely conforming the preform to the mold.

Finally, the stretched material is rapidly quenched against a polished mold surface, which is preferably of at least S.P.I. A-3 grade finish. Such a finish may be produced, for example, with a grade #15 diamond buff.

#### EXAMPLE

The following example is illustrative of the present invention and does not constitute any limitation with regard to the subject matter of the invention.

A Boy 50 ton horizontal injection press, commercially available from Boy Machines Inc., was used to mold a preform of Hoechst A.G. grade 5746 propylene/ethylene

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copolymer resin which is 2.5-3.0% thylene and 97.0-97.5% propylene, and has a melt flow index of about 15. The injection press was outfitted with a 38mm diameter barrel and general purpose screw. The barrel temperature was maintained at about 210°C.

The injection press was run at a 40 second overall injection cycle as follows: the injection fill time was 7 seconds; the injection fill rate was 4.7 grams/sec.; the injection hold time was 7 seconds; and the cooling time was 23 seconds. The mold temperature was maintained at about 5.7°C.

The mold cavity was formed such that a generally cylindrical, hollow preform having a closed end and an open end, and weighing approximately 33g was produced. The preform had a length without finish of 3.59 in., an inner diameter at the main body portion of the preform of 0.778 in., and an outer diameter at the main body portion of the preform of 1.204 in. The preform wall thickness was 0.213 in. at the main body portion, 0.080 in. at the neck, and 0.119 in. at the closed end or endcap.

The preform was allowed to cool to ambient temperature and was transferred to a reheating station. The preform was placed open end down over a mandrel extending vertically from a conveyor. The conveyor indexed about 1.73 inches every 4.58 seconds, carrying the preform between a series of high intensity, quartz tubular IR heating panels (available from Innovative Industries, Inc.) and a parallel reflective shield formed of a highly polished aluminum sheet. Each of the heating panels was disposed generally vertically with the bottom thereof at about the level of the open end of the preform. The

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reflector shield was provided with slots which communicated with a series of cooling air supply ducts. The heating panels and the parallel reflective shield were spaced by about 10 cm, with the conveyor line positioned approximately midway therebetween.

The preform was prerotated for about 18 seconds as it neared the first heating panel, the mandrel rotating at a speed of about 50 to 60 rpm. The preform was then heated for about 41 seconds as it passed by the first heating panel in 9 indexing steps while being continuously rotated. The first heating panel was supplied with 1,000 Watt heaters on a 16 mm center spacing with the following power settings:

|    |         |                          |
|----|---------|--------------------------|
|    | Level 1 | 54.0% (adjacent to neck) |
| 15 | Level 2 | 40.0%                    |
|    | Level 3 | 28.0%                    |
|    | Level 4 | 28.5%                    |
|    | Level 5 | 26.0%                    |
|    | Level 6 | 30.0%                    |
| 20 | Level 7 | 10.0%                    |

While passing by the first heating panel, cooling air at room temperature was directed to the preform through the slots in the reflector shield at a set velocity which was approximately 40% of the capacity of the systems blower.

The preform was then passed beyond the first heating panel to a section of the line devoid of any heating panel, and was thereby cooled for about 18 seconds. Cooling air at room temperature was directed to the preform through the slots in the reflector shield at a set velocity which was approximately 60% of the capacity of the systems blower.

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The preform was then heated for about 41 seconds as it passed by a second heating panel in 9 indexing steps, and while being continuously rotated. The second heating panel was supplied with 1,000 Watt heaters on a 16 mm center spacing with the following settings:

|    |         |                          |
|----|---------|--------------------------|
| 5  | Level 1 | 54.0% (adjacent to neck) |
|    | Level 2 | 40.0%                    |
|    | Level 3 | 28.0%                    |
|    | Level 4 | 28.5%                    |
| 10 | Level 5 | 26.0%                    |
|    | Level 6 | 30.0%                    |
|    | Level 7 | 10.0%                    |

While passing by the second heating panel, cooling air at room temperature was directed to the preform through the slots in the reflector shield at a set velocity which was approximately 40% of the capacity of the systems blower.

The preform was cooled again for about 18 seconds by passing the preform beyond the second heating panel to a section of the line devoid of any heating panel. Cooling air at room temperature was directed to the preform through the slots in the reflector shield at a set velocity which was approximately 60% of the capacity of the systems blower.

The preform was then heated for about 41 seconds in 9 indexing steps in passing by a third heating panel while being continuously rotated. The third heating panel was supplied with 1,000 Watt heaters on a 16 mm center spacing with the following settings:

|    |         |                          |
|----|---------|--------------------------|
| 30 | Level 1 | 47.0% (adjacent to neck) |
|    | Level 2 | 24.0%                    |
|    | Level 3 | 22.0%                    |
|    | Level 4 | 22.0%                    |
|    | Level 5 | 25.0%                    |

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|         |       |
|---------|-------|
| Level 6 | 25.0% |
| Level 7 | 0%    |

While passing by the third heating panel, cooling air at room temperature was directed to the preform through the slots in the reflector shield at a set velocity which was approximately 40% of the capacity of the systems blower.

The preform was cooled again for about 18 seconds by passing the preform beyond the third heating panel to a section of the line devoid of any heating panel. Cooling air at room temperature was directed to the preform through the slots in the reflector shield at a set velocity which was approximately 60% of the capacity of the systems blower.

The mandrel, and thus the preform, was continuously rotated at from about 50 to 60 rpm while advancing through the above described heating and cooling zones. The preform was then transferred to a convection tempering oven set at 135°C for about 27.48 seconds.

The preform was removed from the oven and rapidly transferred to the stretch blow molding apparatus from the RBU 225 system available from Bekum Maschinenfabriken GmbH. The preform was stretch blow molded under the following conditions: the speed of the stretching rod was 0.11 seconds for the full travel of 245 mm; the low pressure setting was 30% of the maximum of about 40 bar; and the low pressure time was 0.11 seconds. Once the stretch rod was fully extended and the preform had been expanded to substantially conform to the mold, a higher pressure of about 70% of the maximum of about 40 bar was applied for about 2.5 seconds to cause the preform to

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completely conform to the mold. The mold temperature was about 5.7°C.

A container of exceptional clarity and good material distribution was obtained.

5        In accordance with the provisions of the patent statutes, the present invention has been described in what is considered to represent its preferred embodiment. However, it should be noted that the invention can be practiced otherwise than as specifically illustrated and  
10       described without departing from its spirit or scope.

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## WHAT IS CLAIMED IS:

1. In a method of injection molding a closed-end preform from a partially crystalline, molecularly orientable plastic for subsequent stretch blow molding, wherein a melt of said material is injected into a preform mold cavity at a predetermined fill rate, the improvement comprising controlling the fill rate to minimize molecular flow orientation induced and the residual stress developed in said plastic material by the injection thereof into the mold, the fill rate being from about 3 grams/second to about 5 grams/second.
2. A method in accordance with claim 1, further comprising the step of rapid quenching after the injection thereof into the preform mold at a cooling rate of from about 4 °C/sec. to about 8 °C/sec.
3. A method in accordance with claim 1, wherein said partially crystalline, molecularly orientable plastic is a polypropylene containing polymer.
4. A method in accordance with claim 3, wherein said partially crystalline, molecularly orientable plastic is a propylene/ethylene copolymer which is greater than 50 percent by weight propylene.
5. A method in accordance with claim 4, wherein said copolymer has a melt flow index of from about 2 to about 50.



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6. A method in accordance with claim 4, wherein said copolymer has a melt flow index of from about 10 to about 30.

5           7. In a method of injection molding a generally cylindrical, hollow preform having a closed end and an open end from a partially crystalline, molecularly orientable plastic for subsequent stretch blow molding, wherein a melt of said material is injected into a preform  
10 mold cavity, the improvement comprising forming said mold cavity so that the resulting preform decreases in thickness at the closed end and the open end of said preform.

15           8. A method in accordance with claim 7, wherein the preform is formed with a decrease in thickness at both the closed end and the open end thereof of between about 40 to 70 percent.

20           9. A method in accordance with claim 8, wherein the preform is formed with a decrease in thickness at both of the ends thereof from about 2 to 4mm.

25           10. A method in accordance with claim 9, wherein said preform is formed with a decrease in thickness at both of the ends thereof of about 3mm.

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11. A closed-end preform of a partially crystalline,  
molecularly orientable plastic for subsequent stretch blow  
molding, the preform comprising an open end and a closed  
end with a generally cylindrical, hollow body portion  
5 there between, the thickness of said body portion  
decreasing at said open end and at said closed end.

12. A preform in accordance with claim 11, wherein  
said partially crystalline, molecularly orientable plastic  
10 is a polypropylene containing polymer

13. A preform in accordance with claim 12, wherein  
said partially crystalline, molecularly orientable plastic  
is a propylene/ethylene copolymer which is greater than 50  
15 percent by weight propylene.

14. A preform in accordance with claim 11, wherein  
said preform is formed with a decrease in thickness at  
both the closed end and the open end thereof of between  
20 about 40 to 70 percent.

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15. A method of reheating a generally cylindrical, hollow preform having a closed end and an open end and formed of a partially crystalline, molecularly orientable plastic prior to stretch blow molding said preform to produce a molded molecularly oriented container, comprising the steps of sequentially:

- 1) exposing said preform to a radiant heat source for a time sufficient to raise the temperature near the outer surface of said preform to a temperature at which intercrystalline structures begin to melt and which approaches but does not exceed the temperature at which all crystal structures near the outer surface of in said preform are melted;
- 2) directing a cooling gas against the exterior of said preform; and
- 3) repeating steps 1 and 2 at least one additional time.

16. A method in accordance with claim 15, wherein subsequent to step 3, said preform is transferred to a convection oven maintained at the final temperature desired for stretch blow molding of the preform.

17. A method in accordance with claim 15, wherein a cooling gas is directed against said preform during step 1.

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18. A method in accordance with claim 17, wherein the velocity of the cooling gas directed against said preform during step 1 is less than the velocity of the cooling gas directed against said preform during step 2.

5

19. A method in accordance with claim 18, wherein the cooling gas directed against said preform during both steps 1 and 2 is comprised of air at ambient temperature.

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20. A method in accordance with claim 15, wherein said radiant heat source is an array of high intensity, quartz tubular IR heaters.

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21. A method in accordance with claim 20, wherein said preform is exposed to infra-red energy of wavelengths of about 1.2 to 1.6 microns.

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22. A method in accordance with claim 15, wherein said preform is heated to a temperature which minimizes the melting of crystal nuclei throughout the wall of the preform.

25

23. A method in accordance with claim 15, wherein said preform comprises an open end and a closed end with a generally cylindrical, hollow body portion there between, the thickness of said body portion decreasing at said open end and at said closed end.

24. A method in accordance with claim 15, wherein said preform is mounted on a conveyor and passed by a series of IR heating panels spaced along the length of said conveyor.

5

25. A method in accordance with claim 24, wherein said preform is mounted on a conveyor and passed by a series of three IR heating panels spaced along the length of said conveyor, the heating panel to which said preform is first exposed being set at a higher power than the power at which at least one of the other of said heating panels is set.

26. A method in accordance with claim 15, wherein angular rotation is imparted to said preform while said preform is being exposed to a source of radiant energy.

27. A method in accordance with claim 26, wherein said preform is provided with angular rotation prior to being exposed to a source of radiant energy.

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28. A method of forming a generally cylindrical, hollow preform having a closed end and an open end and formed of a partially crystalline, molecularly orientable plastic, reheating said preform, and stretch blow molding said preform into conformity with a mold to produce a molded molecularly oriented container, comprising the steps of:

- 1) injection molding said preform;
- 2) cooling said preform to a uniform temperature below its crystal melting point;
- 3) simultaneously:
  - i) passing said preform through a heating zone containing a radiant heat source;
  - ii) imparting angular rotation to said preform while said preform is within said heating zone; and
  - iii) directing a gas which is at a temperature below that which will cause the melting of all crystal structure in said preform to the exterior surface of said preform;
- 4) rapidly transferring said preform to a molding zone and securing said preform within said mold;
- 5) stretching the preform axially with an internal stretch rod which engages the closed end of the preform; and
- 6) creating a pressure differential sufficient to expand the preform into conformity with said mold.

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29. A method in accordance with claim 28, wherein said preform is provided with angular rotation prior to being transferred to said heating zone.

5           30. A method in accordance with claim 28, further comprising the step of removing said preform from said radiant heat zone and directing a cooling gas at a temperature below that which will cause the melting of all crystal structure in said preform against the exterior  
10 surface of said preform, prior to step 4.

          31. A method in accordance with claim 30, further comprising repeating step 3, and then removing said  
15 preform from said radiant heat zone and directing a cooling gas at a temperature below that which will cause the melting of all crystal structure in said preform against the exterior surface of said preform, prior to step 4.

20           32. A method in accordance with claim 31, further comprising the step of introducing said preform into a convection tempering oven which is set at a temperature at which intercrystalline structures in said preform are melted, but which is below the temperature at which all  
25 crystal structures in said preform are melted, allowing any temperature gradient developed across the thickness of said preform to substantially equalize by thermal conduction, and then transferring said preform to said molding zone in step 4.

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33. A method of forming a molded molecularly oriented container, comprising the steps of:

- 1) injection molding a generally cylindrical, hollow preform having a closed end and an open end from a partially crystalline, molecularly orientable plastic, wherein said mold cavity is formed so that the resulting preform decreases in thickness at the closed end and the open end of said preform;
- 2) cooling said preform to a uniform temperature below the temperature at which intercrystalline material in said preform begins to melt;
- 3) simultaneously:
  - i) passing said preform through a heating zone containing a radiant heat source;
  - ii) imparting angular rotation to said preform while said preform is within said heating zone; and
  - iii) directing a cooling gas to the exterior surface of said preform;
- 4) removing said preform from said radiant heat zone and directing a cooling gas against the exterior surface of said preform;
- 5) rapidly transferring said preform to a molding zone and securing said preform within a mold;



1/2

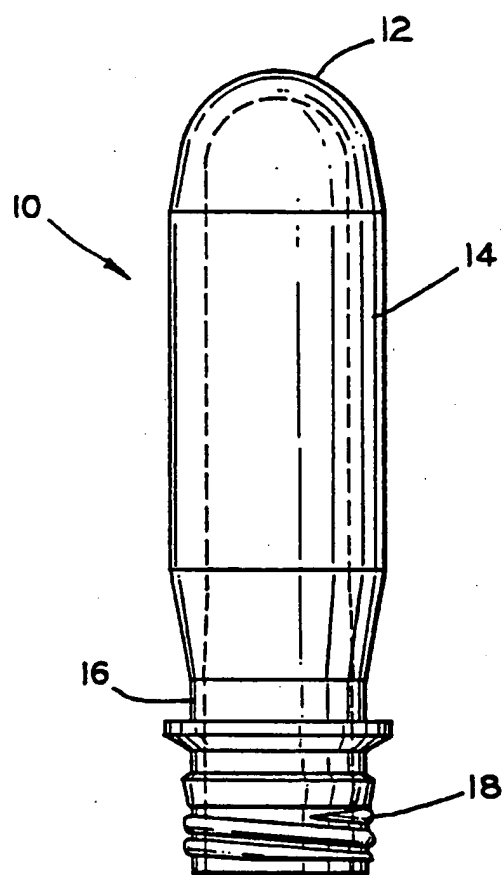


FIG. 1

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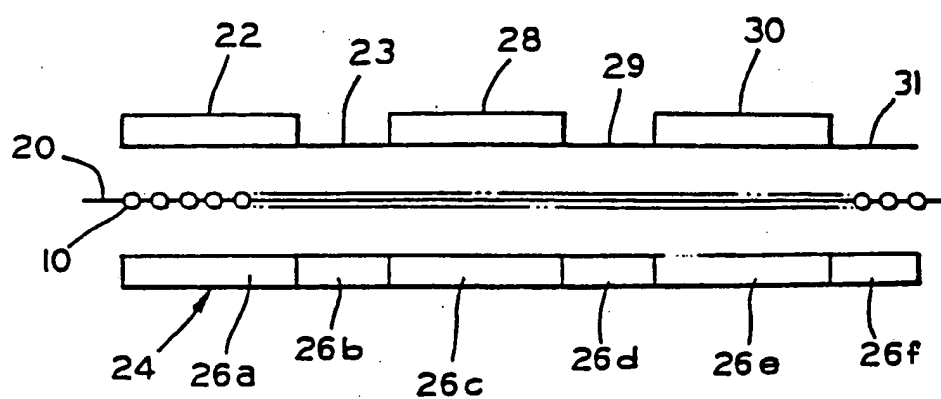


FIG. 2

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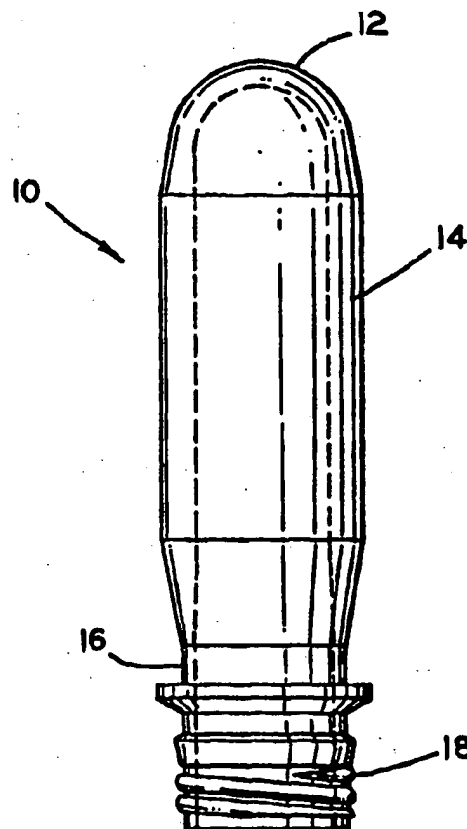
INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

|  |           |   |
|--|-----------|---|
| <p>(51) International Patent Classification <sup>6</sup> :<br/>B29C 45/00, 49/00, 49/64</p>  | <p>A3</p> | <p>(11) International Publication Number: <b>WO 95/11791</b><br/>(43) International Publication Date: 4 May 1995 (04.05.95)</p>   |
| <p>(21) International Application Number: PCT/EP94/03525<br/>(22) International Filing Date: 26 October 1994 (26.10.94)<br/>(30) Priority Data: 08/144,204 27 October 1993 (27.10.93) US<br/>(71) Applicant: BEKUM MASCHINENFABRIKEN GMBH [DE/DE]; Lankwitzer Strasse 14-15, D-12107 Berlin (DE).<br/>(72) Inventors: GITTNER, Franz; Im Grundfeld 33, D-29594 Soltendieck (DE). ROOS, Uwe-Volker; Hasenheide 12, D-29389 Bodenteich (DE). STEELE, Scott, W.; Toledo, Ohio, 1465 Timberwolf Drive, Holland, OH 43528-0964 (US).<br/>(74) Agent: FLOSDORFF, Jürgen; Alleestrasse 33, D-82467 Garmisch-Partenkirchen (DE).</p> |           | <p>(81) Designated States: AU, BR, CA, JP, KR, PL, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).<br/><br/>Published<br/><i>With international search report.<br/>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i><br/>(88) Date of publication of the international search report: 14 September 1995 (14.09.95)</p> |

(54) Title: METHOD OF FORMING MOLECULARLY ORIENTED CONTAINERS

(57) Abstract

The invention relates to a method and apparatus for forming molecularly oriented plastic containers from generally cylindrical, hollow preforms (10) with one open end (18) formed by injection molding from a partially crystalline, molecularly orientable plastic for subsequent stretch blow molding. Melted material is injected into a preform mold at a predetermined fill rate controlled to minimize molecular flow orientation and further controlled to minimize residual stress which both are otherwise developed during injection. The preform (10) is then reheated below the crystal melting point by radiant heat source to a temperature that intercrystalline structures are melted without melting the crystal nuclei. To avoid so-called edge effects resulting from the geometry of the heating zone, the preform decreases in thickness at both (18,12) ends. The preform is then rapidly transferred to the mold in which it is stretched axially with a rod engaging its closed end and then rapidly quenched against a polished mold surface.



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# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/EP 94/03525

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 B29C45/00 B29C49/00 B29C49/64

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 B29C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages   | Relevant to claim No. |
|-----------|--|-----------------------|
| A         | FR,A,2 476 536 (BELOIT CORP) 28 August 1981<br>cited in the application<br>---   | 1,3                   |
| A         | EP,A,0 309 138 (EXXON CHEMICAL PATENTS INC) 29 March 1989<br>see page 4, line 35 - page 5, line 6;<br>figure 1<br>---            | 1,3                   |
| A         | EP,A,0 251 340 (MITSUI TOATSU CHEMICALS) 7 January 1988<br>see page 4, line 14 - line 25<br>see page 5, line 26 - line 31<br>--- | 3-6                   |
| X         | GB,A,2 040 216 (YOSHINO KOGYOSHO CO LTD) 28 August 1980<br>see page 1, line 95 - line 127; figure 1<br>---<br>-/--               | 7,8,<br>11-14         |

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

13 June 1995

Date of mailing of the international search report

17.08.95

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PCT/EP 94/03525

| C(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT |   |                                 |
|---|---|---------------------------------|
| Category *  | Citation of document, with indication, where appropriate, of the relevant passages  | Relevant to claim No.           |
| X   | PATENT ABSTRACTS OF JAPAN<br>vol. 012 no. 131 (M-688), 22 April 1988<br>& JP,A,62 253409 (YOSHINO KOGYOSHO CO<br>LTD) 5 November 1987,<br>see abstract<br>--- | 7-11, 14                        |
| X   | PATENT ABSTRACTS OF JAPAN<br>vol. 012 no. 302 (M-732), 17 August 1988<br>& JP,A,63 078706 (DAINIPPON PRINTING CO<br>LTD) 8 April 1988,<br>see abstract<br>--- | 7-11                            |
| A   | EP,A,0 365 945 (PLASTICON PATENTS) 2 May<br>1990<br>see figures<br>---  | 7-14                            |
| X   | EP,A,0 565 874 (BEKUM MASCHF GMBH) 20<br>October 1993<br>see the whole document<br>---  | 15-20,<br>22, 24-33<br>21, 23   |
| X   | DE,A,31 01 282 (KRUPP CORPOPLAST MASCH) 26<br>August 1982<br><br>see page 6, line 1 - line 22; claims;<br>figures<br>---                                      | 15, 17,<br>19, 20,<br>22, 24-33 |
| X   | FR,A,2 248 131 (HEIDENREICH & HARBECK<br>GMBH) 16 May 1975<br><br>see page 4, line 15 - line 26; claims<br>1, 2, 4, 6-10; figures<br>---                      | 15,<br>17-20,<br>22, 24-33      |
| X   | US,A,4 147 487 (DICKSON ANDREW C ET AL) 3<br>April 1979<br>see column 2, line 3-14; figures 1, 2<br>---   | 15, 20, 21                      |
| A   | EP,A,0 564 354 (S I D E L) 6 October 1993<br>see abstract; figures<br>---   | 15-33                           |
| A   | EP,A,0 500 028 (BEKUM MASCHF GMBH) 26<br>August 1992<br>see abstract; figure<br>-----   | 15-33                           |

# INTERNATIONAL SEARCH REPORT

International application No.

PCT/EP 94/03525

## Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see annex

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☒ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/210

1.- claims 1-6: Method of injection molding a preform comprising controlling the fill rate.

2.- claims 7-14: Method of injection molding comprising using a mold cavity the form of which results in a preform with decreasing thickness at the closed end and at the open end.

claims 15-33: Method of reheating and forming a preform comprising a specific heating and cooling treatment.



# INTERNATIONAL SEARCH REPORT

Information on patent family members

Inter. Appl. Application No  
PCT/EP 94/03525

| Patent document<br>cited in search report | Publication<br>date | Patent family<br>member(s) | Publication<br>date |          |
|---|---------------------|----------------------------|---------------------|----------|
| FR-A-2476536                              | 28-08-81            | US-A-                      | 4357288             | 02-11-82 |
|   |                     | CA-A-                      | 1158821             | 20-12-83 |
|   |                     | DE-A-                      | 3105435             | 02-09-82 |
|   |                     | GB-A, B                    | 2069924             | 03-09-81 |
|   |                     | JP-A-                      | 57039931            | 05-03-82 |
| -----                                     |                     |                            |                     |          |
| EP-A-0309138                              | 29-03-89            | AU-A-                      | 2239088             | 23-03-89 |
|   |                     | JP-A-                      | 1154723             | 16-06-89 |
| -----                                     |                     |                            |                     |          |
| EP-A-0251340                              | 07-01-88            | JP-C-                      | 1734220             | 17-02-93 |
|   |                     | JP-B-                      | 4023620             | 22-04-92 |
|   |                     | JP-A-                      | 60149427            | 06-08-85 |
|   |                     | JP-A-                      | 60125626            | 04-07-85 |
|   |                     | JP-A-                      | 60125627            | 04-07-85 |
|   |                     | JP-A-                      | 60127335            | 08-07-85 |
|   |                     | JP-C-                      | 1837138             | 11-04-94 |
|   |                     | JP-B-                      | 4003727             | 24-01-92 |
|   |                     | JP-A-                      | 60125628            | 04-07-85 |
|   |                     | JP-A-                      | 60127336            | 08-07-85 |
|   |                     | JP-B-                      | 4008211             | 14-02-92 |
|   |                     | JP-A-                      | 60125629            | 04-07-85 |
|   |                     | JP-B-                      | 6039554             | 25-05-94 |
|   |                     | JP-A-                      | 60127337            | 08-07-85 |
|   |                     | JP-C-                      | 1837139             | 11-04-94 |
|   |                     | JP-B-                      | 4003728             | 24-01-92 |
|   |                     | JP-A-                      | 60125630            | 04-07-85 |
|   |                     | JP-A-                      | 60127338            | 08-07-85 |
|   |                     | JP-C-                      | 1730945             | 29-01-93 |
|   |                     | JP-B-                      | 4019925             | 31-03-92 |
|   |                     | JP-A-                      | 60125631            | 04-07-85 |
|   |                     | AU-B-                      | 554076              | 07-08-86 |
|   |                     | AU-A-                      | 3654384             | 20-06-85 |
|   |                     | EP-A-                      | 0151741             | 21-08-85 |
| -----                                     |                     |                            |                     |          |
| GB-A-2040216                              | 28-08-80            | AU-B-                      | 522124              | 20-05-82 |
|   |                     | AU-A-                      | 5454780             | 21-08-80 |
|   |                     | CA-A-                      | 1132465             | 28-09-82 |
|   |                     | CH-A-                      | 641999              | 30-03-84 |
|   |                     | DE-A-                      | 3000102             | 17-07-80 |
|   |                     | FR-A, B                    | 2446712             | 14-08-80 |

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 94/03525

| Patent document<br>cited in search report | Publication<br>date | Patent family<br>member(s)   | Publication<br>date  |
|---|---------------------|--|--|
| GB-A-2040216                              |                     | NL-A- 8000154<br>US-A- 4330579   | 18-07-80<br>18-05-82   |
| EP-A-0365945                              | 02-05-90            | US-A- 4885197<br>US-A- 4950514<br>AU-B- 609326<br>AU-A- 4001789<br>DE-D- 68913263<br>DE-T- 68913263<br>ES-T- 2049296<br>JP-A- 2258214<br>JP-B- 6049328 | 05-12-89<br>21-08-90<br>26-04-91<br>03-05-90<br>31-03-94<br>26-05-94<br>16-04-94<br>19-10-90<br>29-06-94 |
| EP-A-0565874                              | 20-10-93            | DE-A- 4212248<br>JP-A- 6063940<br>US-A- 5326258  | 14-10-93<br>08-03-94<br>05-07-94   |
| DE-A-3101282                              | 26-08-82            | NONE   |  |
| FR-A-2248131                              | 16-05-75            | DE-A- 2352926<br>GB-A- 1483770<br>US-A, B 4076071  | 24-04-75<br>24-08-77<br>28-02-78   |
| US-A-4147487                              | 03-04-79            | US-A- 4079104  | 14-03-78   |
| EP-A-0564354                              | 06-10-93            | FR-A- 2689442<br>JP-A- 6015645<br>US-A- 5322651  | 08-10-93<br>25-01-94<br>21-06-94   |
| EP-A-0500028                              | 26-08-92            | DE-A- 4105403  | 27-08-92   |